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FINAL REPORT - P.I.: Aaron Wold, Department of Chemistry. Brown University

Summary of work done under contract NOOO14-86-K-0234 during the contract period May 1, 1986 to April 30,89 plus the six month extension period ending October 30, 1989.

(See summaries from End-Of-Year Reports 1986, 1987, 1988)

From the 1986 End-of-Year Report

Research in the area of catalysis at Brown deals with the development of low temperature synthetic methods for the preparation of well-dispersed catalysts (Fe_2O_3, Cr_2O_3, Rh_2O_3 and NiO) on several oxide supports (ZrO_2, TiO_2). Physical methods, such as x-ray diffraction, magnetic susceptibility and temperature programmed reduction, are used to study the interaction between the dispersed metal oxide and the support. For the specific system Rh_2O_3/ZrO_2, the solubility of rhodium oxide in the support was followed as a function of the structural changes of the ZrO_2 as well as the stabilization of the Rh_2O_3 towards reduction.

The extent of substitution of nickel into Fe_5C_2 was also studied since both nickel and iron are Fischer-Tropsch catalysts. The limit of substitution was determined for samples prepared under actual reactor conditions and was determined from both magnetic and x-ray analysis.

Finally, a thermomagnetic balance has been constructed and is being used to determine the nucleation and growth of catalytically active magnetic phases which can be correlated at the same time with the temperature programmed reduction data.

From the 1987 End-of-Year Report

During the past year the program underwent a change in direction. The work on the preparation of supported catalysts for the reduction of CO_2 has been phased out and a new effort was started dealing with the chemical properties associated with the preparation and characterization of the new superconducting oxides containing copper. This work has resulted in our repeating what has been done to date so that our effort is at a par with the research being done in other laboratories.

The stability problems associated with the new superconducting oxides have been studied and a number of experiments have been conducted in an attempt to increase stability against CO_2 and water attack.

From the End-of-the-Year Report 1988

The project presently deals with the preparation of complex oxides of copper in order to ascertain the effect of the A-site ion on the superconducting properties of substituted La_2CuO_4 and $Ba_2YCu_3O_7$. The investigation is being extended to other oxides of copper, e.g. $Y_2Cu_2O_5$ and $La_2CaCu_2O_6$. In addition, an effort has been started on the growth of thin films of superconductors by the use of spray pyrolysis. Spray pyrolysis, spin coating, and evaporated films seem to be the three viable techniques for the preparation of well-characterized thin films of the various copper superconductors.

In addition to the above information the following applies to work done during the balance of the contract time period:

Samples of $La_{2-x}Bi_xCuO_4$ were prepared by codecomposition of the nitrates in air. Single phase products were obtained for $x \leq 0.10$. The substitution of bismuth for lanthanum resulted in an increase in delocalization of holes, as indicated by increased conductivity and a decrease in the Neél temperature. Samples were also annealed in argon at 600°C and their properties compared with the samples as prepared in air.

The substitution of lead and cadmium for lanthanum in La_2CuO_4 was studied and the limites of solubility were established. Single phase compositions were characterized and their physical properties were correlated with the substitution of bismuth and are interpreted on the basis of a model proposed by Goodenough.

Members of the system $La_{2-x}A_{1+xx}\ Cu2O_{6+y}$ where A = Ca,Sr were prepared by decomposition of the nitrates. The tolerance of these compounds for oxygen uptake, as well as the substitution for the A-site ions, is shown to be closely related to the distribution of the alkali earth ions on the 8- and 9-coordinated A-sites.

See Technical Reports 1-23

Technical Report 1. Preparation and Characterization of Nickel Substituted Fe_5C_2; May 1986.

Technical Report 2. Preparation and Characterization of Members of the Chromium-Zirconium Oxide System; January 1987.

Technical Report 3. Preparation and Properties of Dispersed Iron(III) Oxide on Rutile; January 1987.

Technical Report 4. An Examination of the Relative Stabilities of $Mg_xNi_{1-x}O$ and NiO on Spherocarb

Technical Report 5. Preparation and Properties of Cubic ZrO_2 Stabilized with Ni(II); May 1987.

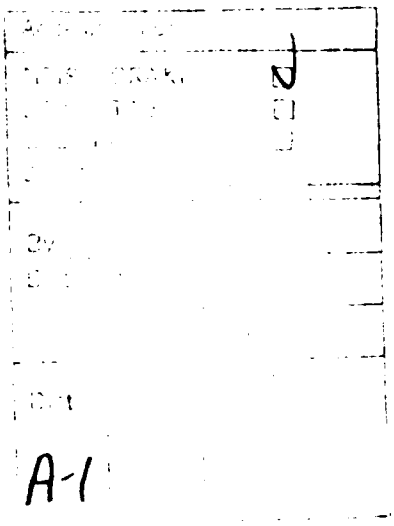
Technical Report 6. Stabilization of Cubic ZrO_2 with Rh(III) and/or La(III); May 1987.

Technical Report 7. Preparation and Characterization of Cubic ZrO_2 Stabilized by Fe(III) amd Fe(II) May 1987.

Technical Report 8. Study of the Oxidation State of Copper in $La_{1.8}Sr_{.2}CuO_4$; June 1987.

Technical Report 9. Preparation and Characterization of Co(II)/ZrO_2Solid Solution; October 1987.

Technical Report 10. Preparation and Characterization of Thin Films of Alumina by Metalorganic Chemical Vapor Deposition; October 1987



Technical Report 11. Chemical Problems Associated with the Preparation and Characterization of Superconducting Oxides Containing Copper; October 1987.

Technical Report 12. Preparation and Characterization of $Ba_2YCu_3O_{7.01}$(2); October 1987.

Technical Report 13. Preparation and Properties of the System $Cr_{2-x}Rh_xO_3(2 \geq x \geq 0)$; January 1988

Technical Report 14. Preparation and Characterization of ZrO_2 Stabilized with Ru(IV) and La(III); January 1988.

Technical Report 15. Determination of the Homogeneity Range of La_2CuO_4; July 1988.

Technical Report 16. Preparation and Characterization of $Cd_{1-x}Fe_xSe$ Single Crystals; July 1988.

Technical Report 17. Preparation and Characterization of Members of the Systems Cu(II) MgO/Cu(II)ZrO_2; December 1988.

Technical Report 18. Preparation and Properties of $La_{2-x}Bi_xCuO_4(.1 \geq x \geq 0)$; December 1988.

Technical Report 19. Preparation and Properties of $La_{2-x}A_xCuO_{4-y}$ Where A = Pb,Cd; April 1989

Technical Report 20. Preparation and Characterization of Members of the System $La_{2-x}A_{1+x}Cu_2O_{6\pm y}$ Where A = Ca,Sr; May 1989

Technical Report 21. Preparation and Characterization of Several Concudtion Transition Metal Oxides; May 1989

Technical Report 22. Preparation and Characterization of Cu(II) Oxide; May 1989.

Technical Report 23 Preparation and Characterization of Copper(II) Oxide Single Crystals by Chemical Vapor Transport; May 1989

(Note: Technical Reports 20-23 overlap with new ONR contract but research was begun under this contract and reports made accordingly.)

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